

**Soil/Sediment Design Comparison (15%) Study
Oxidation Addendum**

**Standard Chlorine of Delaware Site
New Castle County, Delaware**

**USEPA Work Assignment No. 038-RDRD-03H6
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Introduction

Contamination from the former Standard Chlorine of Delaware (SCD) manufacturing facility has spread through the underlying soil and groundwater to impact Red Lion Creek, the unnamed tributary of Red Lion Creek, and the wetlands surrounding both water bodies. To address this contamination, the March 9, 1995 Record of Decision (ROD) specified the use of ex-situ low temperature thermal desorption (LTTD) for treatment of the impacted soils and sediments. During the Design Comparison Study (DCS) conducted by Black & Veatch Special Projects Corporation (BVSPC), it was determined that the volumes of soil and sediment requiring treatment using the ROD-specified remedial approach would be substantially greater than those anticipated at the time the ROD was put in place.

This increased treatment volume resulted from both a greater than expected area of wetlands contamination and a greater than expected depth to which treatment will be required in the wetlands. Deterioration of the silt fence that was installed at the northern end of the tributary following the 1986 tank failure has allowed site-related contaminants to spread northward beyond this fence line towards the Red Lion Creek. In addition, while the 1993 Feasibility Study (FS) Report projected that only the top one foot of sediments from the tributary wetlands would require treatment, sampling conducted as part of BVSPC's Remedial Design (RD) effort showed that site-related contaminants were present to an average depth of between six and seven feet below ground surface (bgs). This increased contamination depth is most likely attributable to downward migration of the contaminants in the years since the Remedial Investigation (RI) was conducted in the early 1990s.

Based on the results of the RD investigation effort, it was estimated that approximately 130,000 cubic yards of soils and sediments would require excavation and treatment as compared to the approximate 32,400 cubic yards initially estimated in the FS Report. Because LTTD costs are generally calculated on a per ton basis, this larger volume resulted in a substantial increase in the estimated overall remedial project costs for the site. Anticipated project costs were further impacted by the increased site preparation and dewatering activities that would be required for excavation of the deeper contaminated wetlands sediments and soils.

In addition, because of the presence of an operating facility at the site, the ROD-specified remedial approach did not directly address deep contaminated subsurface soils located beneath the facility. Instead, the ROD addressed the groundwater contamination that would be caused by these soils. While this approach will be effective in the long term,

EPA believes that it would be preferable to identify a cost-effective in-situ method for eliminating the contaminants from the soil and groundwater (if one exists).

Consequently, EPA requested that BVSPC perform a preliminary review of available in-situ treatment technologies that might hold the potential to reduce the overall cost of remediation at the SCD site. In particular, EPA is interested in determining if any such technologies that were not commercially available at the time of the ROD might have application at this site.

Following an initial review of various in-situ technologies, BVSPC identified in-situ oxidation as a technology that holds particular promise for addressing the wetlands and deep subsurface soil and groundwater contamination at the SCD site. Since its first field applications in the 1990s, this technology has become an increasingly popular method of in-situ treatment of subsurface organic contamination.

Technology Overview

In-situ chemical oxidation involves the injection of a chemical oxidant (e.g., hydrogen peroxide, ozone, permanganate) into the contaminated area through injection wells, Geoprobe-mounted injectors, or some other method. When the injected oxidant comes in contact with an organic contaminant, it reacts rapidly to break the chemical bonds of the compound and resulting intermediaries.

Previously published research (Watts et al, 1997; Watts et al, 1994; Sedlak and Andren, 1991) has shown that hydrogen peroxide can be successfully used to chemically oxidize chlorinated benzene compounds. In this research, oxidation of the chlorobenzene compounds was found to occur according to first order kinetics with rate constants decreasing for more chlorinated compounds and generally increasing with higher concentrations of hydrogen peroxide. When investigating hematite (a naturally occurring iron oxide commonly found in soils) catalyzed oxidation of chlorobenzene compounds with hydrogen peroxide, Watts et al (1997) found that with the exception of hexachlorobenzene, oxidation of sorbed chlorobenzene compounds generally occurred at hydrogen peroxide concentrations greater than 2%. When investigating oxidation of hexachlorobenzene on soil with Fenton's reagent (hydrogen peroxide mixed with ferrous iron), Watts et al (1994) observed oxidation of sorbed hexachlorobenzene when soluble iron and hydrogen peroxide concentrations exceeded approximately 3,300 mg/l. The above-referenced research projects both found that oxidation of dissolved phase chlorobenzene compounds occurred even at much lower hydrogen peroxide concentrations.

Sedlak and Andren also found that oxidation with Fenton's reagent could achieve

complete mineralization of chlorobenzene and all intermediary compounds within hours and that oxidation was optimized at pH values between 2 and 3. This is primarily due to the fact that this is the range where maximum soluble ferrous iron levels are obtained. Vendors have noted that subsequent field, pilot, and treatability studies have shown that use of chelating agents increases the soluble ferrous iron concentration and thus eliminates or reduces the need to adjust the pH to these lower levels.

In addition to this research, pilot and field scale projects carried out by commercial vendors have been successful in addressing chlorobenzene contamination. Geo-Cleanse International, Inc. reported an average 82% reduction within nine months (actual time for injections was approximately 45 days) in groundwater chlorobenzene and dichlorobenzene concentrations during a three phase oxidation program at the Charleston Naval Complex (Geo-Cleanse, 2002). In-Situ Oxidative Technologies, Inc. reported 98% destruction of chlorinated benzene compounds within six months in groundwater at a quarry/truck maintenance facility in Sussex County, NJ (ISOTEC, 1998).

The information supplied in the above-referenced studies/projects and discussions with vendors and other authorities on the technology revealed that the effectiveness of a chemical oxidation project is impacted by a number of site-specific factors.

Hydrogeologic properties of a site can impact the number of injection points and rounds of injections. Because the oxidant must contact the contaminant to achieve treatment, oxidation is usually accomplished more easily in soils with higher permeability (e.g., sands) than in low permeability soils such as clays or tight bedrock. Similarly, in-situ oxidation is typically more cost-effective when employed in the saturated zone – where groundwater helps spread the oxidant – than in the vadose zone.

As might be expected, the chemistry of the soils being treated also has a substantial impact on the effectiveness of chemical oxidation. Soils with high levels of organic matter (as determined by total organic carbon [TOC]) require greater amounts of oxidant to complete the remedial action. This is because Fenton's reagent is a non-specific oxidant and will oxidize both the contaminant-related and non-contaminant organic matter. In addition, high levels of manganese and ferric iron – which act as oxidation catalysts – and carbonates (alkalinity) – which act as hydroxyl scavengers – can also increase the amount of oxidant needed for the project. Conversely, high levels of naturally occurring ferrous iron can reduce the necessary volume of the iron-based catalyst required for the oxidation process.

With regard to long-term impacts on the soil being treated, in-situ oxidation with hydrogen peroxide is considered to be relatively benign. Aside from decreasing the

organic content of the soils and increasing the iron and chloride concentration in the treated soils, it is not anticipated that the treatment chemicals themselves would have any negative impact on the wetlands area. Treatment process intermediary compounds – such as chlorophenols, dichlorobiphenyls, and chlorobenzoquinone – should be oxidized to carbon dioxide, water and chloride along with the chlorobenzene compounds.

Potential Treatment Method and Costs

Based on initial discussions with vendors, it is expected that the most cost-effective method of injecting the Fenton's reagent (with chelating agents) in the tributary wetlands will be through the use of a Geoprobe-mounted injection system. To ensure access to the projected injection points, it is anticipated that a series of temporary roads would have to be built on the wetlands.

It is anticipated that the wetlands injectors will be screened between three to five and eight feet bgs to achieve treatment of the entire depth of contamination. Vendors have expressed differing degrees of concern regarding the relatively shallow nature of the wetlands contamination and the potential for short-circuiting to occur. One vendor felt that while short-circuiting would most likely decrease the radius of influence for each injection, it would generally not pose a substantial problem and shallower contamination would be addressed as the oxidant rose to the surface from the injection zone. Another vendor suggested that it might be necessary to overlay the injection area with a geomembrane and three to five feet of sand to address short-circuiting in the wetlands. The shallow nature of the contamination – combined with the high levels of organic material at the wetlands surface – mean that some temporary foaming could be observed in the wetlands during the treatment process.

To address the deep subsurface contamination underlying the facility, vendors suggested that injection wells be used to deliver the Fenton's reagent/chelating agent mixture. These wells would be screened from the groundwater level (approximately 40 feet bgs) down to the clay layer that underlies the SCD Site. The use of in-situ oxidation in these areas would serve the dual purpose of addressing the soil contamination and treating the contaminant plume in the groundwater.

In both the wetlands and uplands areas, it is estimated that injections will be spaced every 30 feet and that three or more rounds of injections will be required to fully remediate the contaminated area. Both the number of injections and their spacing are only preliminary estimates that must be updated as additional site-specific testing is conducted.

Based on initial estimates of treatment chemical volumes and injection points it is projected that the treatment of the wetlands area would cost between approximately \$3

million and \$5 million. Treatment of the deep soils underlying the facility would most likely cost between approximately \$2 million and \$4 million. It is also projected that the actual treatment of the contaminated areas (once the initial testing is completed and the approach is approved) could be completed in less than a year. These figures are very preliminary and should be used with extreme caution.

Suggested Approach

Because the potential success of in-situ chemical oxidation is highly dependent on site-specific conditions, it is imperative that treatability and pilot-scale studies be conducted before any full-scale treatment is attempted. Therefore it is recommended that a series of treatability studies be performed utilizing contaminated soil collected from the SCD Site. Although various treatment vendors are capable of performing these tests, it would be preferable – to eliminate any appearance of a conflict of interest – to have an independent laboratory with experience in chemical oxidation research perform these studies.

One lab that has performed extensive research in this area (and specifically with chlorobenzene oxidation) is located at Washington State University and is headed by Dr. Richard Watts. Dr. Watts has stated that treatability tests would cost approximately \$2,000 per sample and would require the collection of a ½ gallon sample of soil or a one gallon sample of groundwater for each test. Treatment vendors have stated that similar treatability tests would cost between \$5,000 and \$10,000 per sample. To obtain a good picture of the potential for using oxidation at SCD, it is suggested that a series of samples – collected from different locations with varying concentrations – be tested.

It is also recommended that soil samples be collected from five to ten locations across the wetlands and analyzed for parameters including sulfates, alkalinity, pH, TOC, and chlorides. One to three groundwater samples should also be collected and analyzed for oxidation reduction potential, total dissolved solids, ferrous iron, and turbidity. Subsurface samples could also be collected from facility locations and similarly analyzed. The results of these analyses would allow potential treatment vendors to more precisely identify dosing and injection requirements and provide more accurate pilot-study cost estimates.

Based on the results of the treatability studies, it would then be necessary to undertake a pilot-scale test during which a small portion of the contaminated area would be treated. This test would necessarily be performed using an oxidation remediation contractor and would give a better picture of the potential for the technology to address the site-specific conditions. Vendors have stated that a pilot test of this type would cost approximately \$100,000 to complete. Because of the variations in contaminant levels and potential

treatment terrain (wetlands versus upgradient), it might be necessary to perform more than one of these tests.

Summary

Based on referenced projects and discussions with available vendors, it appears that in-situ chemical oxidation – if properly implemented – has the potential to quickly oxidize chlorinated benzene compounds to relatively harmless byproducts including carbon dioxide and water. Although some initial investment would be required to better gauge the potential effectiveness of this treatment approach, the graduated approach suggested will allow the EPA to determine whether in-situ oxidation has application at this particular site without committing the resources necessary for a full-scale treatment.

Given the potential to reduce the overall remedial action cost and to shorten the time to site restoration, it is recommended that the use of chemical oxidation at SCD be investigated further.

References

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